Chapter 10
Gases
Characteristics of Gases

• Unlike liquids and solids, they
  ➢ Expand to fill their containers.
  ➢ Are highly compressible.
  ➢ Have extremely low densities.
• Substances that are solids or liquids under ordinary conditions can exist as gases too.

• In that state they are referred as vapors.

• Water vapor.
• Gases form homogeneous mixtures regardless of their identities.

• Non miscible liquids in their vapor form are totally homogenous mixtures.

• For example water and gasoline that are not miscible in each other, mix completely in their vapor form.
• This is because of the fact that the gas molecules are so far apart they do not influence each other.
Pressure

- Pressure is the amount of force applied to an area.
  \[ P = \frac{F}{A} \]
- Atmospheric pressure is the weight of air per unit of area.
Units of Pressure

- **Pascals**
  - $1 \text{ Pa} = 1 \text{ N/m}^2$

- **Bar**
  - $1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa}$

\[
1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa} = 1 \text{ Bar}
\]
Units of Pressure

- mm Hg or torr
- Atmosphere
  - $1.00 \text{ atm} = 760 \text{ torr}$
Manometer

Used to measure the difference in pressure between atmospheric pressure and that of a gas in a vessel.

\[ P_{\text{gas}} = P_{\text{atm}} + P_h \]
Standard Pressure

• Normal atmospheric pressure at sea level.

• It is equal to
  ➢ 1.00 atm
  ➢ 760 torr (760 mm Hg)
  ➢ 101.325 kPa
Boyle’s Law
(1627-1691)

The volume of a fixed quantity of gas at 
*constant temperature* is inversely proportional 
to the pressure.
Boyle’s Law
\[ V \propto \frac{1}{P} \quad \Rightarrow \quad V = \text{Constant} \times \frac{1}{P} \]

\[ PV = \text{constant} \]

- The value of the constant depends on the temperature and the amount of gas in the sample.
As $P$ and $V$ are inversely proportional

Since $PV = k$

$V = k \left(\frac{1}{P}\right)$

This means a plot of $V$ versus $1/P$ will be a straight line.
Charles’s Law \((1787)\)

Jacques Charles 1746-1823

- The volume of a fixed amount of gas at constant pressure is directly proportional to its absolute temperature.

\[ V \propto T \]

\[ V = kT \]

The value of \( k \) depends on pressure and the amount of gas.

- i.e., \( \frac{V}{T} = k \)

A plot of \( V \) versus \( T \) will be a straight line.
Lord Kelvin  
(William Thomson)  
(1824- 1907)

1848 He proposed the Kelvin scale  
0 K is -273.15 °C  
0 K is the temperature at which all atomic motion comes to a complete stop.
Gay- Lussac

- He was interested in lighter than air balloons.
- He made an ascent in a balloon to 23,000 ft.
- This is the interest that led him to study the properties of gases.
• He explained the law of combining volumes.
• At given T and P the gases that react with each other are in ratios of whole numbers.

\[
\begin{align*}
\text{Observation} & \quad \text{Two volumes hydrogen} & \quad \text{One volume oxygen} & \quad \text{Two volumes water vapor} \\
\text{Explanation} & \quad \begin{array}{c}
\includegraphics[width=0.2\textwidth]{hydrogen_dihydrogen.png} \\
\includegraphics[width=0.2\textwidth]{oxygen_dioxide.png} \\
\includegraphics[width=0.2\textwidth]{water_vapor.png}
\end{array} & \quad \text{\rightarrow} & \quad \text{\rightarrow} \\
\text{Equation} & \quad 2 \text{H}_2(\text{g}) & + & \text{O}_2(\text{g}) & \rightarrow & 2 \text{H}_2\text{O}(\text{g})
\end{align*}
\]
Avogadro’s Hypothesis

- Equal volumes of gases at the same temperature and pressure contain equal number of molecules.
- At 0°C and 1 atm pressure 22.4 L of any gas has $6.02 \times 10^{23}$ (one mole) molecules.
<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>N₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>22.4 L</td>
<td>22.4 L</td>
<td>22.4 L</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
<td>1 atm</td>
<td>1 atm</td>
</tr>
<tr>
<td>Temperature</td>
<td>0°C</td>
<td>0°C</td>
<td>0°C</td>
</tr>
<tr>
<td>Mass of gas</td>
<td>4.00 g</td>
<td>28.0 g</td>
<td>16.0 g</td>
</tr>
<tr>
<td>Number of gas molecules</td>
<td>$6.02 \times 10^{23}$</td>
<td>$6.02 \times 10^{23}$</td>
<td>$6.02 \times 10^{23}$</td>
</tr>
</tbody>
</table>
Avogadro’s Law

- The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas.

- \( V \propto n \)
- \( V = kn \)
Ideal-Gas Equation

• So far we’ve seen that

\[ V \propto \frac{1}{P} \] (Boyle’s law)
\[ V \propto T \] (Charles’s law)
\[ V \propto n \] (Avogadro’s law)

• Combining these, we get

\[ V \propto \frac{nT}{P} \]
The relationship

\[ V \propto \frac{nT}{P} \]

then becomes

\[ V = R \frac{nT}{P} \]

or

\[ PV = nRT \]
Ideal-Gas Equation

\[ R = \frac{PV}{nT} \]

The constant of proportionality is known as \( R \), the gas constant.

- PV has the unit of energy

<table>
<thead>
<tr>
<th>Units</th>
<th>Numerical Value</th>
</tr>
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<tbody>
<tr>
<td>L-atm/mol-K</td>
<td>0.08206</td>
</tr>
<tr>
<td>J/mol-K*</td>
<td>8.314</td>
</tr>
<tr>
<td>cal/mol-K</td>
<td>1.987</td>
</tr>
<tr>
<td>m³·Pa/mol-K*</td>
<td>8.314</td>
</tr>
<tr>
<td>L-torr/mol-K</td>
<td>62.36</td>
</tr>
</tbody>
</table>

*SI unit.
\[ V = \frac{nRT}{P} \]

\[ P = 1.000 \text{ atm} \]
\[ n = 1.000 \text{ mole} \]
\[ T = 0.00 \degree \text{C} = 273.15 \text{ K} \]

\[ V = (1.000 \text{mole}) \times (0.08206 \text{ L atm/mol-K}) \times (273.15 \text{K}) \]

\[ 1.000 \text{ atm} \]

\[ = 22.41 \text{ L} \]
• $0^\circ \text{C}$ and 1 atm are referred to as standard temperature and pressure (STP).

• 22.41 L is the molar volume of gas at STP
The image shows a bar graph comparing the molar volumes of various gases. The gases listed are:

- Ideal gas: 22.41 L
- Cl₂: 22.06 L
- CO₂: 22.31 L
- NH₃: 22.40 L
- N₂: 22.40 L
- He: 22.41 L
- H₂: 22.42 L

The graph indicates that the molar volume of the ideal gas is the highest at 22.41 L, followed by others, with H₂ having the second-highest volume at 22.42 L.
Ideal Gas

• Ideal gas is a hypothetical gas whose pressure, volume and temperature behavior is completely followed by the ideal gas equation.
Calcium carbonate, CaCO$_3$(s), decomposes upon heating to give CaO(s) and CO$_2$(g). A sample of CaCO$_3$ is decomposed, and the carbon dioxide is collected in a 250-mL flask. After the decomposition is complete, the gas has a pressure of 1.3 atm at a temperature of 31°C. How many moles of CO$_2$ gas were generated?
• Tennis balls are usually filled with air or N₂ gas to a pressure above atmospheric pressure to increase their “bounce.” If a particular tennis ball has a volume of 144 cm³ and contains 0.33 g of N₂ gas, what is the pressure inside the ball at 24°C?
1) In a Torricelli barometer, a pressure of one atmosphere supports a 760 mm column of mercury. If the original tube containing the mercury is replaced with a tube having twice the diameter of the original, the height of the mercury column at one atmosphere pressure is __________ mm.
• Chapter 10: 10.9, 10.13, 10.17, 10.21, 10.23, 10.25, 10.29, 10.31, 10.35, 10.39 [Answer to part b is 9.41 L], 10.43, 10.47, 10.53, 10.55, 10.57, 10.59, 10.63, 10.65, 10.69, 10.73, 10.77, 10.79, 10.801, 10.81, 10.105.
Relating the Ideal Gas Equation and the Gas Law

• $PV = nRT$
• When the temperature and the quantity of the gas are kept constant
  $PV = \text{Constant}$
This is Boyle’s law.
  So
  $P_1 V_1 = P_2 V_2$
\[ \frac{P}{T} = \frac{nR}{V} \text{ constant} \]

\[ \frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ and so on} \]

\[ \frac{PV}{T} = nR = \text{constant} \]

\[ \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \]
The gas pressure in an aerosol can is 1.5 atm at 25°C. Assuming that the gas inside obeys the ideal-gas equation, what would the pressure be if the can were heated to 450°C?
A large natural-gas storage tank is arranged so that the pressure is maintained at 2.20 atm. On a cold day in December when the temperature is –15°C (4°F), the volume of gas in the tank is 28,500 ft³. What is the volume of the same quantity of gas on a warm July day when the temperature is 31°C (88°F)?
Densities of Gases

If we divide both sides of the ideal-gas equation by $V$ and by $RT$, we get

$$\frac{n}{V} = \frac{P}{RT}$$
Densities of Gases

• We know that
  moles $\times$ molecular mass = mass

$$\text{moles} \times \frac{\text{grams}}{\text{moles}} = \text{gram}$$

$$n \times M = m$$

• So multiplying both sides by the molecular mass ($M$) gives

$$\frac{Mn}{V} = \frac{PM}{RT}$$

$$\frac{m}{V} = \frac{PM}{RT}$$
Densities of Gases

• Mass / volume = density

• So,

\[ d = \frac{m}{V} = \frac{PM}{RT} \]

• Note: One only needs to know the molecular mass, the pressure, and the temperature to calculate the density of a gas.
Molecular Mass

We can manipulate the density equation to enable us to find the molecular mass of a gas:

\[ d = \frac{PM}{RT} \]

Becomes

\[ M = \frac{dRT}{P} \]
What is the density of carbon tetrachloride (CCl₄) vapor at 714 torr and 125°C?
The mean molar mass of the atmosphere at the surface of Titan, Saturn’s largest moon, is 28.6 g/mol. The surface temperature is 95 K, and the pressure is 1.6 atm. Assuming ideal behavior, calculate the density of Titan’s atmosphere.
A series of measurements are made in order to determine the molar mass of an unknown gas. First, a large flask is evacuated and found to weigh 134.567 g. It is then filled with the gas to a pressure of 735 torr at 31°C and reweighed; its mass is now 137.456 g. Finally, the flask is filled with water at 31°C and found to weigh 1067.9 g. (The density of the water at this temperature is 0.997 g/mL.) Assuming that the ideal-gas equation applies, calculate the molar mass of the unknown gas.
Volume of Gases in Chemical Reactions

The safety air bags in automobiles are inflated by nitrogen gas generated by the rapid decomposition of sodium azide, \( \text{NaN}_3 \):

\[
2 \text{NaN}_3(s) \rightarrow 2 \text{Na}(s) + 3 \text{N}_2(g)
\]

If an air bag has a volume of 36 L and is to be filled with nitrogen gas at a pressure of 1.15 atm at a temperature of 26.0°C, how many grams of \( \text{NaN}_3 \) must be decomposed?
Dalton’s Law of Partial Pressures

• The total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone.

• In other words,

\[ P_{\text{total}} = P_1 + P_2 + P_3 + \ldots \]
A gaseous mixture made from 6.00 g O₂ and 9.00 g CH₄ is placed in a 15.0-L vessel at 0°C. What is the partial pressure of each gas, and what is the total pressure in the vessel?
• Total Pressure $P_t = P_1 + P_2 + P_3 \ldots \ldots$ 

$$PV = nRT$$

and $P = \frac{nRT}{V}$

$P_1 = \frac{n_1RT}{V} \quad ; \quad P_2 = \frac{n_2RT}{V} \quad \text{and so on} \ldots \ldots$

$$P_t = \frac{(n_1+n_2+n_3 \ldots \ldots)RT}{V} = nt \left(\frac{RT}{V}\right)$$

The total pressure at constant $T$ and $V$ is determined by the total number of moles of gas present, it is not important if it is just one gas or a mixture of many gases.
Partial Pressure and Mole Fractions

- \( P = \frac{nRT}{V} \)

As each gas in a mixture behaves independently we can relate the amount of the given gas in a mixture with its partial pressure.

\[
P_1 = \frac{n_1RT}{V} = n_1
\]

\[
P_t = \frac{n_tRT}{V} = n_t
\]

\[
P_1 = \left(\frac{n_1}{n_t}\right)P_t
\]

\[
n_1/n_t \text{ is called the mole fraction } X
\]

So \( P_1 = X_1 P_t \)

- Mole fraction \( X \) = moles of component total moles of all the components
From data gathered by *Voyager 1*, scientists have estimated the composition of the atmosphere of Titan, Saturn’s largest moon. The total pressure on the surface of Titan is 1220 torr. The atmosphere consists of 82 mol percent N\textsubscript{2}, 12 mol percent Ar, and 6.0 mol percent CH\textsubscript{4}. Calculate the partial pressure of each of these gases in Titan’s atmosphere.

\[ P_1 = X_1 P_t \]
Partial Pressures

- When one collects a gas over water, there is water vapor mixed in with the gas.

\[ P_{\text{total}} = P_{\text{gas}} + P_{\text{H}_2\text{O}} \]

- To find only the pressure of the desired gas, one must subtract the vapor pressure of water from the total pressure.

\[ P_{\text{gas}} = P_{\text{total}} - P_{\text{H}_2\text{O}} \]

\( P_{\text{H}_2\text{O}} \) at that temperature will be given to you.
A sample of KClO$_3$ is partially decomposed (Equation 10.16), producing O$_2$ gas that is collected over water. The volume of gas collected is 0.250 L at 26°C and 765 torr total pressure. (a) How many moles of O$_2$ are collected? (b) How many grams of KClO$_3$ were decomposed?

$$2\text{KClO}_3 (s) \rightarrow 2\text{KCl} (s) + 3\text{O}_2 (g)$$

a) $P_{\text{gas}} = P_{\text{total}} - P_{\text{H}_2\text{O}}$

then calculate $n$ with $n = \frac{PV}{RT}$ for O$_2$

Then for b) do the stoichiometric calculation.
Kinetic-Molecular Theory

This is a model that aids in our understanding of what happens to gas particles as environmental conditions change.
Main Tenets of Kinetic-Molecular Theory

Gases consist of large numbers of molecules (or atoms) that are in continuous, random motion.
Main Tenets of Kinetic-Molecular Theory

• The combined volume of all the molecules of the gas is negligible relative to the total volume in which the gas is contained.

• Attractive and repulsive forces between gas molecules are negligible.
Main Tenets of Kinetic-Molecular Theory

Energy can be transferred between molecules during collisions, but the *average* kinetic energy of the molecules does not change with time, as long as the temperature of the gas remains constant.
Main Tenets of Kinetic-Molecular Theory

The average kinetic energy of the molecules is proportional to the absolute temperature.
• The pressure of the gas is caused by the collision of the molecules with the walls of the cylinder. The magnitude of the pressure depends on the frequency and the force of the collisions.

• The temperature of the gas depends on the average kinetic energy of the molecules.
- At higher temperatures a large fraction of molecules move at a greater speed.
- Root mean square (rms) speed.
  \[ \sqrt{\frac{1}{4} (4.0^2 + 6.0^2 + 10.0^2 + 12.0^2)} = \sqrt{74.0} = 8.6 \text{ m/s} \]

- Average speed
  \[ \frac{1}{4} (4.0 + 6.0 + 10.0 + 12.0) = 8.0 \text{ m/s} \]
• The average kinetic energy related to the rms

\[ \varepsilon = \frac{1}{2}mv^2 \]

• As KE increases with temperature, so does the rms speed (and of course the average speed)
Application to the gas law

Effect of volume increase at constant $T$

- KE is constant
- rms will remain constant
- If $V$ increases the volume travels a longer distance between collisions
- This results in fewer collisions and hence lower pressure.

This is Boyle's Law
Effect of T increase at constant V

- KE increases
- rms increases
- More collisions
- Hence higher pressure.

This is Charles Law
Molecular Effusion and Diffusion

• The KE of any gas particle is a specific value at any given temperature
• It does not matter what the identity of the gas particle is, its energy would still be the same value
• In such a case the particle with the higher mass would have lower rms speed.
The following equation expresses the relationship between the rms speed and the molar mass of the particles of gas:

$$u = \sqrt{\frac{3RT}{M}}$$

(we will not be doing the derivation of this equation)
Effusion

The escape of gas molecules through a tiny hole into an evacuated space.
Diffusion

The spread of one substance throughout a space or throughout a second substance.
Graham’s Law of Effusion

The effusion rate of a gas is inversely proportionate to the square root of its molar mass.

If \( r \) is the rate of effusion and \( M \) is the molar mass,

\[
r \propto \frac{1}{\sqrt{M}}
\]
• If we have two gases and the rate of their effusion is \( r_1 \) and \( r_2 \) and their molar masses are \( M_1 \) and \( M_2 \) then according to Graham’s law

\[
\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}
\]

If the rate if effusion of two gases is compared it is seen that the lighter gas effuses more rapidly.
• Rate of effusion is directly proportionate to the rms speed of the molecule.

\[ \frac{r_1}{r_2} = \frac{u_1}{u_2} \]
Graham's Law of Effusion

The effusion rate of a gas is inversely proportional to the square root of its molar mass. Gas effuses through pores of a balloon. At identical pressure and temperature, the lighter gas effuses more rapidly.

Two balloons are filled to the same volume, one with helium and one with nitrogen.

After 48 hours, the helium-filled balloon is smaller than the nitrogen-filled one because helium escapes faster than nitrogen.

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An unknown gas composed of homonuclear diatomic molecules effuses at a rate that is only 0.355 times that of \( \text{O}_2 \) at the same temperature. Calculate the molar mass of the unknown, and identify it.
Diffusion and Mean Free Path

Diffusion like effusion is faster for lower mass molecules.
Molecular collision makes diffusion more complicated than effusion.
Even though the speed of molecules at room temperature is very high, the molecules take a long time to diffuse because of the molecular collisions.
• Average distance traveled by a molecule between collisions is called the **mean free path**.
PV = nRT
n = \frac{PV}{RT}

• For one mole of gas at any pressure
  \frac{PV}{RT} = n = 1
In the real world, the behavior of gases only conforms to the ideal-gas equation at relatively high temperature and low pressure.
• The real gases do have some volume and have some attraction for one another
• At high pressure the volume of the gases becomes significant and the attractive forces come into play
• At low temperature the molecules are deprived of the energy they need to overcome their mutual attraction
Deviations from Ideal Behavior

The assumptions made in the kinetic-molecular model break down at high pressure and/or low temperature.
Corrections for Nonideal Behavior

• The ideal-gas equation can be adjusted to take these deviations from ideal behavior into account.

• The corrected ideal-gas equation is known as the van der Waals equation.
van der Waal introduced two constants $a$ and $b$ to make the corrections.
The van der Waal Equation

\[(P + \frac{n^2a}{V^2}) (V - nb) = nRT\]
Gases

- Larger molecules not only have larger volumes, they also have greater intermolecular attractive forces.

<table>
<thead>
<tr>
<th>Substance</th>
<th align="right">$a$ (L$^2$-atm/mol$^2$)</th>
<th align="right">$b$ (L/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td align="right">0.0341</td>
<td align="right">0.02370</td>
</tr>
<tr>
<td>Ne</td>
<td align="right">0.211</td>
<td align="right">0.0171</td>
</tr>
<tr>
<td>Ar</td>
<td align="right">1.34</td>
<td align="right">0.0322</td>
</tr>
<tr>
<td>Kr</td>
<td align="right">2.32</td>
<td align="right">0.0398</td>
</tr>
<tr>
<td>Xe</td>
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<td>H$_2$</td>
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<td align="right">0.0266</td>
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<td>N$_2$</td>
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<tr>
<td>O$_2$</td>
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<tr>
<td>Cl$_2$</td>
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<td>CO$_2$</td>
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<tr>
<td>CCl$_4$</td>
<td align="right">20.4</td>
<td align="right">0.1383</td>
</tr>
</tbody>
</table>
10.16 If 1.000 mol of an ideal gas were confined to 22.41 L at 0.0°C, it would exert a pressure of 1.000 atm. Use the van der Waals equation and the constants in Table 10.3 to estimate the pressure exerted by 1.000 mol of Cl2(g) in 22.41 L at 0.0°C.